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(54) Preparation of monochloro-olefins by oxychlorination of alkanes

(57) A process for the production of monochlorinated olefin comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising (1) metallic silver and/or a compound thereof and (2) one or more compounds of manganese, cobalt or nickel. It is useful for the production of vinyl chloride from ethane.

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SPECIFICATION

Production of monochlorinated compounds

The present process relates to the production of monochlorinated compounds by the oxychlorination of alkanes.

Vinyl chloride is at present manufactured in an essentially two stage process by the oxychlorination of ethylene. Since ethane is potentially a much cheaper feedstock there is considerable incentive to devise a suitable alternative process, particularly if a single stage process can be developed.

Several possible processes have been disclosed (e.g. US 3,937,744; Ger Off 2,540,067; US 3,629,351). In general these employ similar catalysts to those employed for ethylene oxychlorination (i.e. copper based) but it is generally found that much higher reaction temperatures are required (450—600°C as compared with about 300—350°C). This is a serious disadvantage since the catalyst can be molten or partially volatile (necessitating a complex reactor design) and the highly corrosive reaction conditions require the use of expensive construction materials.

We have now discovered certain catalysts which can operate in a temperature regime substantially below that hitherto possible and thus reduce corrosion/erosion problems. The catalysts may be used in the solid particulate state, thus avoiding reactor problems associated with molten salts and permitting the use of both fixed and fluid bed reactors. These catalysts thus afford the advantage of a selective single stage process based on ethane feedstock.

According to the present invention we provide a process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising (1) metallic silver and/or a compound thereof and (2) one or more compounds of manganese, cobalt or nickel.

The components (1) and (2) comprising the catalyst composition may be present in physical admixture or in chemical combination with one another.

The catalyst may include components other than (1) and (2), for example copper oxide, copper chloride and lanthanides.

The process of the invention is applicable to a range of alkane starting materials, especially alkanes having 2 to 4 carbon atoms, for example ethane. The starting material may comprise an alkane/alkene mixture. The alkene may be, for example, ethylene, propylene and various butenes.

The process of the invention is especially applicable to the production of vinyl chloride from ethane or ethane/ethylene mixtures.

As already mentioned, the silver may be incorporated into the catalyst composition as metal but it will be appreciated that under the reaction conditions metallic silver may be converted wholly or in part to the chloride or oxychloride (or to the corresponding oxide).

The compound of silver (component (1) of the catalyst composition) and the compounds of manganese, cobalt or nickel (component (2) of the catalyst composition) which compounds may be the same or different are suitably present as oxides (which may be converted under the reaction conditions to the corresponding chlorides and/or oxychlorides), and/or chlorides and/or oxychlorides. Compounds of the catalyst components such as nitrates, carbonates, hydroxides, phosphates, and acetates may also be employed which may be converted to oxides, chlorides, oxychlorides or mixtures thereof under the reaction conditions. Component (1) and/or component (2) may also be present in the form of a cation exchanged zeolite.

A preferred catalyst composition comprises metallic silver and/or silver oxide, chloride, oxychloride or mixtures thereof and manganese oxide, chloride or oxychloride or mixtures thereof. Conveniently, the preferred catalyst composition may comprise initially silver oxide and/or metallic silver and manganese oxide, which as already mentioned may at least partially be converted to the corresponding chlorides and/or oxychlorides under the reaction conditions. In an especially preferred catalyst of silver and manganese, X-ray diffraction identified the major phases present before catalytic reaction as silver metal and $AgMn_2O_4$ while for an especially preferred combination of silver and cobalt, the major precursor phase was found to be $AgCoO_2$ (delafossite structure).

It is preferred to employ catalysts having atomic ratios of silver to one or more of the metals, manganese, cobalt and nickel in the range from 10:1 to 1:10 more preferably from 3:1 to 1:3, for example 1:1, except in the case of cation exchanged zeolites where this range may be much wider, for example from 50:1 to 1:50. The catalyst may conveniently be prepared by coprecipitation of the compounds, e.g. oxides comprising components (1) and (2) which coprecipitation may be effected chemically, thermally or electrically, or by a combination of these methods. Suitably, the coprecipitation consists in preparing a solution containing the materials from which the desired components e.g. oxides can be precipitated. Alternatively the catalysts may be prepared by sintering the components or by combining the molten components.

The catalyst may be supported if desired on known carriers such as, for example, silica, alumina, various zeolites or titania. The surface area of the support can be varied widely but is usually in the range 0.1 to 50 m^2/g.

The supported catalyst may be employed in fixed, moving or fluidised beds of the appropriate size.

When using a zeolite as a support, the catalyst may conveniently by prepared by impregnating or exchanging the zeolite with cations or oxides of silver and manganese, cobalt or nickel.

The reaction temperature may vary according to the reactant employed. Suitably, for example for the reaction of ethane or ethane/ethylene, the reaction temperatures are in the range 250°C—475°C, for example 300°C—400°C. The reaction is normally carried out under atmospheric or superatmospheric pressure, e.g. at a pressure in the range 1 to 100 bars.

The source of oxygen may be oxygen itself or oxygen enriched air. The molar ratios of alkane (and alkene when present) and oxygen are preferably in the range 0.1 to 10 moles of oxygen for each mole of alkane and alkene, for example 0.5 to 2 moles of oxygen for each mole of alkane and alkene.

The source of chlorine is suitably chlorine itself or a mixture of chlorine and hydrogen chloride, or a mixture of chlorine and chlorinated hydrocarbons (e.g. chlorohydrocarbons such as ethyl chloride, ethylene dichloride). It is preferred to use chlorine or a mixture of chlorine and hydrogen chloride (including ammonium chloride which on heating decomposes to give hydrogen chloride). Typically, the reaction mixture contains 0.1 to 10 moles of chlorine, for example 1 to 3 moles of chlorine for each mole of alkane and alkene.

The products of the reaction may be isolated and used as such or, if desired, may be recycled wholly or partially to the reactor in order to increase the yield of monochlorinated olefin, e.g. vinyl chloride.

The invention is illustrated by the following Examples.

EXAMPLE 1

A catalyst containing equal atomic proportions of silver and manganese was prepared by coprecipitation from the nitrates. A solution of 17 g of silver nitrate dissolved in 22 ml of water was mixed with 43 ml of 50% manganous nitrate solution and slowly added to a solution of 28 g of NaOH dissolved in 100 ml of water boiling under reflux in a nitrogen atmosphere. Refluxing was continued for 5 hours and after cooling, the black precipitate was filtered off, washed with water until alkali free and then with 25% NH_4OH solution. After further washing until alkali free, the filtrate was dried at 120°C and heated from 200°C to 450°C over a period of 5 hours. Finally the catalyst was calcined for 16 hours at 450°C. After grinding to 250—500 μm mesh size, the catalyst was loaded into a 6.3 mm O.D. tubular microreactor (equipped with an on-line GLC system) to give a bed length of 10 cm. The catalyst was pretreated in a current of chlorine for one hour at 300°C. Catalytic performance was then assessed under varying gas feed conditions and over a range of temperatures, product analyses being performed by on-line GLC.

By varying the contact time at a constant reaction temperature of 400°C and with a feed ratio of air:ethane:chlorine of 5:1:1 the results were obtained as shown in Table 1.

Varying the ratio of ethane to chlorine at the same temperature gave the results shown in Table 2.

EXAMPLE 2

A catalyst containing silver and manganese in the atomic ratios 1:2 was prepared, pretreated and tested as in Example 1 to give results at 400°C as shown in Table 3.

EXAMPLE 3

A catalyst containing 12.1 wt% silver and 0.6 wt% manganese was prepared by exchanging 4.3 g of the sodium form of offretite zeolite with 10 ml of an aqueous solution containing 33% manganous nitrate and 1.5 g of silver nitrate. After washing and drying at 120°C the catalyst was calcined at 450°C for 16 hours and tested as in Example 1 with a gas feed consisting of 10 ml/min air, 2 ml/min ethane and 2 ml/min chlorine. The results are shown in Table 4.

EXAMPLE 4

A catalyst was prepared as in Example 2 but including 10 atom % lanthanum as the nitrate in the solution of nitrates. The results obtained at 400°C are shown in Table 5.

EXAMPLE 5

A catalyst containing equiatomic proportions of silver and cobalt was prepared as in Example 1 but substituting cobaltous nitrate for manganous nitrate solution. Catalytic results at 400°C are presented in Table 6.

TABLE 1

Contact time secs	Ethane Conversion mol %	Selectivity (%)									
		VC	CO_2	C_2H_4	EtCl	CH_4	MeCl	1.1 Di	EDC	β-Tri	VDC
0.5	79.7	13.6	0.4	13.7	58.4	1.0	1.8	5.9	2.3	0.1	0.2
1.0	98.0	29.7	1.8	22.2	29.5	2.4	1.7	4.1	5.2	0.5	0.5
2	98.3	17.4	5.3	36.9	21.4	8.3	3.4	2.2	3.8	–	0.5
3.5	99.8	32.3	3.9	33.7	11.1	5.2	2.2	1.6	5.4	1.2	1.6
5	100	32.7	6.9	37.9	3.4	8.1	2.7	0.5	4.0	–	1.3
10	99.7	23.9	11.7	36.3	2.9	15.8	4.8	0.1	1.5	0.5	0.4

TABLE 2

Ethane Air Cl_2 ml/min			Product Selectivity %									
			VC	CO_2	C_2H_4	EtCl	CH_4	MeCl	EDC	Tri	β-Tri	VDC
2	10	2	23.8	3.7	28.8	23.5	9.2	3.2	4.4	0.1	0.8	0.6
2	10	6	41.5	0.8	2.7	1.2	–	0.2	12.8	2.2	24.2	6.7

NOTES ON TABLES 1—6

VC	=	vinyl chloride	$CH_2{=}CHCl$
1,1 Di	=	β-dichloroethane	CH_3CHCl_2
EDC	=	ethylene dichloride	CH_2ClCH_2Cl
β-Tri	=	trichloroethane	$CH_2ClCHCl_2$
VDC	=	vinylidene dichloride	$CH_2{=}CCl_2$
Tri	=	trichloroethylene	$CHClCCl_2$

Trans dichlor = Trans dichloroethylene $C_2H_2Cl_2$ (trans)
Cis dichlor = Cis dichloroethylene $C_2H_2Cl_2$ (cis)
DCM = Dichloromethane

TABLE 3

Feed Gas Flows mls/min Air	Ethane	Cl_2	Conversion (C_2H_6 mol %)	Selectivity (%) VC	CO_2	C_2H_4	CH_4	MeCl	EtCl	VDC	EDC	β-Tri
15	3	3	99.7	28.5	7.2	33.1	10.8	3.5	8.0	1.1	4.3	1.1
15	3	4	100	38.3	5.7	25.2	6.8	2.6	6.6	1.6	7.1	2.3
15	3	6	100	51.0	2.8	15.9	1.9	1.2	3.7	5.4	8.8	4.0
5	1	0.5	98.7	22.0	8.7	33.5	12.9	3.1	1.7	0.6	9.0	5.4
5	1	2	100	46.4	1.6	4.4	0.8	0.4	0.4	15.7	6.0	5.4

TABLE 4

Reaction Temp °C	Ethane Conversion mol %	Selectivity (%) VC	CO_2	C_2H_4	EtCl	MeCl	Trans Dichlor	Cis Dichlor	EDC	β-Tri
325	61.9	18.6	17	19.9	1.8	1.0	2.6	6.0	25.5	6.4
350	67.3	32.1	12.5	14.0	0.8	1.2	5.2	13.8	16.7	2.8
375	74.2	35.6	9.6	18.2	0.7	1.0	5.7	16.0	10.9	1.4
400	83.9	35.5	10.0	30.6	0.7	0.8	4.6	12.6	3.6	0.6

TABLE 5

Gas Feed mls/min			Conversion (Ethane mol %)	Selectivity (%)									
Ethane	Air	Cl_2		VC	CO_2	C_2H_4	CH_4	EtCl	MeCl	EDC	Cis Dichloro	Tri	β-Tri
2	10	2	100	24.9	–	–	9.4	15.3	10.2	34.0	1.0	0.2	2.0
2	10	4	100	41.3	–	–	6.4	3.4	4.4	30.4	5.3	1.1	3.0
2	10	6	100	40.1	–	–	2.3	3.8	2.0	32.8	5.4	2.0	5.9

TABLE 6

Gas Feed mls/min			Conversion (Ethane mol %)	Selectivity (%)								
Ethane	Air	Cl_2		VC	CO_2	C_2H_4	EtCl	EDC	Trans Dichloro	MeCl	DCM	β-Tri
10	50	10	28	11	7	10	60	7	–	2	–	–
10	50	15	56	10	4	16	61	2	2	4	2	–
5	50	15	95	16	7	11	40	11	8	3	3	–
2.5	50	17.5	100	21	6	5	19	19	12	2	5	7

CLAIMS

1. A process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising (1) metallic silver and/or a compound thereof and (2) one or more compounds of manganese, cobalt or nickel.

2. A process according to claim 1 wherein the alkane is ethane.

3. A process according to claim 1 or claim 2 wherein the catalyst composition comprises at least one of metallic silver, silver oxide, silver chloride and silver oxychloride and at least one of manganese oxide, manganese chloride and manganese oxychloride.

4. A process according to any one of the preceding claims wherein the catalyst composition is such that the atomic ratio of silver to one or more of the metals manganese, cobalt and nickel is in the range from 10:1 to 1:10.

5. A process according to claim 4 wherein the atomic ratio of silver to one or more of the metals manganese, cobalt and nickel is in the range from 3:1 to 1:3.

6. A process according to any one of the preceding claims wherein the gaseous mixture contains from 0.1 to 10 moles of oxygen for each mole of alkane.

7. A process according to claim 6 wherein the gaseous mixture contains from 0.5 to 2 moles of oxygen for each mole of alkane.

8. A process according to any one of the preceding claims wherein the gaseous mixture contains from 0.1 to 10 moles of chlorine for each mole of alkane.

9. A process according to claim 8 wherein the gaseous mixture contains from 1 to 3 moles of chlorine for each mole of alkane.

10. A process according to claim 1 substantially as hereinbefore described with reference to the foregoing Examples.

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